Question I, 24 points (6 points each): True or False: Provide a brief justification or no credit.

a) What is $\ln(10^6!)$ to two significant figures?
\[ \sim 10^6 \ln (10^6) = 10^6 \approx 1.3 \times 10^7. \]

b) The total differential of enthalpy may be written $dH = TdS + VdP + \mu dN$. Three Maxwell relations follow from this expression. What are they?
\[ \frac{\partial T}{\partial P} \bigg|_S = \frac{\partial V}{\partial S} \bigg|_P, \quad \frac{\partial T}{\partial N} \bigg|_P = \frac{\partial \mu}{\partial S} \bigg|_P, \quad \frac{\partial V}{\partial N} \bigg|_S = \frac{\partial \mu}{\partial P} \bigg|_S. \]

c) Suppose that you wanted to define a new thermodynamic potential that was a natural function of the variables $(S, P, \mu)$ and you call the potential $\Pi(S, P, \mu)$. Write down an expression for this potential and for the total derivative of this potential in terms of variations in its natural variables.
\[ \Pi = U + PV - \mu N \quad \text{or} \quad \Pi = TS \]
\[ d\Pi = TdS + VdP - Nd\mu \]

d) The function $f(x, y, z)$ is homogeneous of order one and the function $g(x, y)$ is homogeneous of order zero. If we know that $f(1, 5, 3) = 6$ and that $g(1, 5) = 3$, what are the following:
\[ f(3, 15, 9) = 18 \]
\[ g(1/2, 5/2) = 3 \]

Question II, 20 points: You throw a 1 kilogram hot (400K) block of solid lead (Pb) into a swimming pool. The water in the pool starts out at 300 K. Assume the swimming pool is so large that the lead is unable to change the temperature of the water and assume that the swimming pool (including both the lead and the water) is thermally isolated from the rest of the universe and is held at a constant pressure of 1 atm. Calculate ΔS\text{Pb}, ΔS\text{water}, ΔS\text{universe}. What is the final temperature of the lead and how do you know that the change to this final state will actually happen?

The specific heat capacity of lead is 0.150 J g⁻¹ K⁻¹
The specific heat capacity of water is 4.184 J g⁻¹ K⁻¹

\[ q_{\text{Pb}} = C_{\text{Pb}} \Delta T = 0.150 \frac{J}{g \cdot K} \times 1000 \ g \times (400 - 300) K = -15000 \ J \]

\[ q_{H_2O} = -q_{\text{Pb}} = +15 \ KS \]

\[ \Delta S_{H_2O} = \frac{q_{H_2O}}{T_{H_2O}} = \frac{15000 \ J}{300 \ K} = 50 \frac{J}{K} = \Delta S_{H_2O} \]

\[ \Delta S_{\text{Pb}} = \int_{300K}^{400K} \frac{C_{\text{Pb}} \ dT}{T} = C_{\text{Pb}} \ln\left(\frac{300}{400}\right) = 0.150 \frac{J}{g \cdot K} \times 1000 \ g \times \ln(0.75) \]

\[ \Delta S_{\text{Pb}} = -43.2 \ J/K \]

\[ \Delta S_{\text{Pb}} + \Delta S_{H_2O} = \Delta S_{\text{universe}} = +6.8 \ J/K \]

Final temp of Pb is 300 K.
The change will happen since ΔS\text{universe} > 0
and the process is spontaneous.
Question III, 20 points: I suggest you read all parts of this problem before beginning.

In class, we started our discussion about the statistical basis of entropy with the system of an ideal gas. We first guessed that the number of microstates for the gas had the following form:

$$\Omega(N,V,U) = \left(\frac{V}{V_0}\right)^N$$

where

$$V_0 = \left[ 3\frac{\hbar^2}{4e^{\pi}U} \right]^\frac{3}{2}$$

is predicted by quantum mechanics. ($h$ is Planck’s constant, $e$ is Euler’s number and $m$ is the mass of a single gas molecule.)

a) (5 pts.) This expression must be flawed from a thermodynamic perspective since it yields a ridiculous prediction about the entropy of an ideal gas. What is the incorrect prediction? (You have to explain in words what the problem is. Do not simply write down an expression for $S$ here.)

Predicts a non-extensive entropy.

b) (5 pts.) What is the correct expression for $\Omega(N,V,U)$ that fixes this flaw and what is the physical basis for the correction.

$$\Omega_{\text{corr}} = \frac{1}{N!} \left(\frac{V}{V_0}\right)^N$$

The $k$'s are $\frac{1}{N!}$ because

the gas particles

indistinguishable.

c) (10 pts.) Show explicitly how the expression from part b leads to reasonable behavior for the entropy, whereas the incorrect expression provided to you leads to the problem discussed in part a.

$$\ln\left(\frac{1}{N}\right) = -Nk_bN + N = -Nk_bN + Nk_b\epsilon$$

$$S_{\text{corr}} = k_b \ln \Omega_{\text{corr}} = k_b \left[ -Nk_bN + Nk_b\epsilon + Nk_b\left(\frac{V_0}{N}\right) \right]$$

$$S_{\text{corr}} = Nk_b \ln\left(\frac{V_0}{N}\right)$$

is extensive since term in ( ) is intensive.

$$S_{\text{corr}} = k_b \ln \Omega_{\text{corr}} = k_b Nk_b\epsilon \left(\frac{V_0}{N}\right) \leftarrow \text{this is super-extensive}$$

it behaves like $Nk_b N$
Question IV, 36 points (12 points each): These are derivations. Show your work or no credit.

a) Starting from the definition $C_v = \frac{\partial U}{\partial T}_{V,N}$, derive the equivalent alternate expression $C_v = T \frac{\partial S}{\partial T}_{V,N}$.

\[
C_v = \frac{\partial U}{\partial T}_{V,N} = \frac{\partial U}{\partial S}_{V,N} \frac{\partial S}{\partial T}_{V,N} = T \frac{\partial S}{\partial T}_{V,N}
\]

\[\text{Chain rule} \quad \frac{\partial U}{\partial S}_{V,N} = T \quad \text{from}
\]

\[\Delta U = T \Delta S - p \Delta V + \mu \Delta N
\]

b) Express $C_p - C_v$ in terms of the thermodynamic quantities $\beta, \kappa, T, V$.

\[
\frac{\partial S}{\partial T}_p = \frac{\partial S}{\partial T}_V + \frac{\partial S}{\partial V}_T \frac{\partial V}{\partial T}_p
\]

\[\text{N is a fixed constraint or "fix your gun" "cliff Eastwood"}
\]

\[
\frac{\partial S}{\partial T}_p - \frac{\partial S}{\partial T}_V = \frac{\partial P}{\partial T}_V \frac{\partial V}{\partial T}_p
\]

\[\text{Maxwell relation}
\]

\[
= \beta \kappa \frac{\partial P}{\partial T}_V
\]

\[\text{\beta \kappa \frac{\partial V}{\partial T}_p}
\]

\[\text{\beta \kappa \frac{\partial V}{\partial T}_p}
\]

\[\kappa V = - \frac{\partial P}{\partial T} \quad \&
\]

\[C_p - C_v = T \left( \frac{\partial S}{\partial T}_p - \frac{\partial S}{\partial T}_V \right) = \frac{T \beta^2 V}{\kappa}
\]

Part c on next page...
c) The multiplicity of a large Einstein solid with \( N \) oscillators and \( q \) units of energy is given by 
\[
\Omega(N,q) = \frac{(q+N-1)!}{q!(N-1)!}
\]
Show that this result implies that the entropy of an Einstein solid is 
\[
S(N,q) = k_B N \ln \left( \frac{qe}{N} \right)
\]
when both \( N \) and \( q \) are very large and, additionally, that \( q \gg N \). (\( e \) is Euler's number)

\[
\Omega \approx \frac{(q+N)!}{q! N!} q^N \quad \text{"up to \( k_B \)%" so can ignore the \( k_B \)}
\]

\[
\zeta = k_B n_s \Rightarrow S \approx k_B n_s
\]

\[
S \approx k_B \left[ (q+N) \ln(q+N) - (q+N) - q \ln q + q \right. - N \ln N + N
\]

\[
= k_B \left[ q \ln \left( \frac{q+N}{q} \right) + N \ln \left( \frac{q+N}{N} \right) \right]
\]

\[
\downarrow \ln(1+x) = x \quad \downarrow q \gg N
\]

\[
\approx k_B \left[ q \left( \frac{N}{q} \right) + N \ln \left( \frac{q}{N} \right) \right]
\]

\[
= k_B \left[ N \ln e + N \ln \left( \frac{92}{N} \right) \right]
\]

\[
\boxed{S \approx k_B N \ln \left( \frac{qe}{N} \right)}
\]